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NAVAL STRUCTURAL MATERIALS: REQUIREMENTS, ISSUES, AND OPPORTUNI--ETC(U)
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REPORT DOCUMENTATION PAGE AD-A095 724

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: NRL Memorandum Report 4484	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER: Memorandum rept.
4. TITLE (and Subtitle): NAVAL STRUCTURAL MATERIALS: REQUIREMENTS, ISSUES, AND OPPORTUNITIES	5. TYPE OF REPORT & PERIOD COVERED: Topical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): L. R. Hettche and A. I. Schindler	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Naval Research Laboratory, Washington, DC 20375	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 66356/6010
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Arlington, VA 22217	12. REPORT DATE: 8 — 10 April 1981
	13. NUMBER OF PAGES: 37
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

6, 10, 11 10 Apr 81, 12 37

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for presentation at the North Atlantic Treaty Organization (NATO)/Defense Research Group (DRG) Seminar on Advances in Structural Materials in Relation to Defense Applications.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Naval structural material	Crack tolerant properties	Corrosion	Particle injection
High performance ships	Ion implantation	Surface properties	
V/STOL aircraft	Laser surface modification	Surface alloying	
Naval vehicles	Fracture	Wear	
Crack tolerant properties	Fatigue	Friction	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This paper presents selective examples of requirements, issues, and opportunities associated with naval structural materials. In particular, the relationships between operational capabilities and structural material requirements are examined for the following Naval systems: future high performance ships, next generation V/STOL aircraft, and conventional ships. These systems are selected for review because of the differences in their time frames for operational deployment.

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20. Abstract (Continued)

Because of paper length consideration, the discussions on technical issues and R&D opportunities are limited respectively to high strength marine alloys and emergent surface modification techniques of ion implantation and laser beam processing. Here the ability to control and predict an exacting trade off in engineering properties and service behavior is identified as a key technical issue in developing improved alloy systems. Moreover, ion implantation and laser beam processing offer the capability to optimize independent surface and bulk properties without the discontinuous interface of conventional coatings as well as to minimize the use of scarce or otherwise expensive materials. These discussions provide examples of structural materials development at various stages of technological maturity and therefore at various proximities from system impact.

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NAVAL STRUCTURAL MATERIALS: REQUIREMENTS, ISSUES, AND OPPORTUNITIES

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INTRODUCTION

Improvements in structural materials technology over the remainder of this century pose one of the more important and certainly one of the most challenging areas of Naval research and development. This forecast is based, in part, on the findings of a recently completed investment strategy for management of the U.S. Navy's materials R&D resources. Developed under the aegis of the Chief of Naval Development, this study, the so called Materials Technology Strategy, identified potential impact of materials technology on Navy and Marine Corps operational capabilities, as well as deficiencies and R&D opportunities.

Foremost among these findings is the pervasive and often critical role structural materials play in defining the military effectiveness of Naval vehicles and weapon systems. Most often, the development of new and improved operational capabilities is dependent in varying degrees on the development of new and improved structural materials. In addition, there are urgent requirements for structural materials and production techniques which will improve availability, damage tolerance and survivability, while reducing cost of most major systems. Finally, critical materials availability, energy conservation, and environmental and safety regulations are emergent issues which will place increasing demands on future structural materials technology.

Another strategy indicator of the potential impact of structural material technology on future systems comes from the pairing of key technical issues and R&D opportunities. Here, the picture which emerges is one of accelerated application of the interdisciplinary approach of modern material science to the development of new and improved structural materials technology and the accelerated transfer of this technology to the design, fabrication, and maintenance schedule of future systems. In many ways, our ability to supply improved and innovative structural materials in a timely and affordable way will be an important factor in determining the types, numbers, and mix of future vehicles and platforms.

In accordance with the strategy rationale, this paper presents selective examples of requirements, issues, and opportunities associated with naval structural materials. In particular, the relationships between operational

Manuscript submitted February 6, 1981.

capabilities and structural material requirements are examined for the following Naval systems: future high performance ships, next generation V/STOL aircraft, and conventional ships. These systems are selected for review because of the differences in their time frames for operational deployment. Because of paper length consideration, the discussions on technical issues and R&D opportunities are limited respectively to high strength marine alloys and emergent surface modification techniques of ion implantation and laser beam processing. Here the ability to control and predict an exacting trade off in engineering properties and service behavior is identified as a key technical issue in developing improved alloy systems. Moreover, ion implantation and laser beam processing offer the capability to optimize independent surface and bulk properties without the discontinuous interface of conventional coatings as well as to minimize the use of scarce or otherwise expensive materials. These discussions provide examples of structural materials development at various stages of technological maturity and therefore at various proximities from system impact.

From the admittedly incomplete survey of topics covered in this paper, it is hoped that the diversity and complexity of the challenges facing the Navy's structural materials community over the next several decades will become manifest.

STRUCTURAL MATERIAL REQUIREMENTS OF SELECTED NAVAL SYSTEMS

High Performance Ships

High performance hydrofoils, surface effect ships (SES), air cushion vehicle (ACV) and other advanced vehicles utilized structural and machinery materials to their performance limits. The primary operational utility of these vehicles in comparison with conventional ships is their high speeds and in some cases enhanced sea-keeping behavior. Depending on the lift and installed horsepower of various designs, these vehicles have demonstrated and projected speeds in the range of 50 to 100 knots. However, because of the high horsepower and high specific fuel consumption, the payloads of these vehicles are penalized relative to conventional designs. The so-called useful load (fuel and payload) of advanced ships, approximately 50% of the full gross weight, is strongly dependent on the structural weight fraction and to a lesser extent on machinery and lift system weights. Accordingly, the operational capabilities of advanced ships are dependent on the availability of high performance structural materials.

To date, advanced ships built by the U.S. Navy have been test and evaluation platforms (SES-100 and PCH-1 hydrofoil) and special purpose craft (PHM hydrofoil) of 50 to 200 tons. The hull structures of these craft are predominantly welded construction of 5000 marine series aluminum alloys. The struts and foils of hydrofoils have utilized a variety of high strength alloys, including HY-steels, PH stainless steels, and titanium. Although materials problems have appeared in these applications, the general materials performance is judged as adequate.

By contrast to existing vehicles, far-term (Circa 2000) advanced ship designs are perceived as large (1,000 to 10,000 ton), high speed (50-100 knot) open ocean combatants. As indicated by the structural weight fraction vs. gross tonnage trends of Fig. 1, the advanced design concepts appear as near-level extrapolation of the smaller existing vehicles; and in fact, the advanced designs are based on current structural materials and fabrication technology. Because structural efficiency is expected to increase with size, it could be concluded that the advanced vehicles are conservatively designed with regard to structural weight and structural integrity. However, this conclusion is premature for any one of several factors.

As high value combat platforms, the advanced concepts must contain a greater degree of damage tolerance than existing vehicles. These requirements include ballistic armor (directly substituted in the SWES-100 structural weight) and fire barrier protection of the aluminum structure. Hence, in order to incorporate the added damage tolerance requirements without sacrifice of operational performance in future large high performance ships, some combination of the following improvements must be effected: (1) reduction in weight of structural and machinery components; and/or (2) use of materials in a multifunctional design-e.g., integrated structure/armor/fire-barrier material.

Also implicit in the design approach of large high performance ships is the assumption that operational loads can be defined to an accuracy approaching that used in modern aerospace design. Indeed, the advanced ship design concepts are not unlike those used in a modern air transport (e.g., C-5A) predominantly of aluminum construction with a gross take off weight of approximately 300 tons, and a structural weight fraction between 0.35 and 0.40. However, high performance ships do not have the benefit of the highly redundant, crack arresting features of aircraft riveted construction. In the all welded aluminum construction of high performance ships, precise load information is required to ascertain the adequacy of current design practices and criteria for potentially severe loading conditions such as low cycle fatigue. Moreover, load definition and material performance for large, high performance vehicles cannot be inferred with a high degree of confidence from the design and operational experiences of much smaller vehicles. Hence, design optimization and structural life management concepts will require considerable R&D efforts, including adequate lead time and experience with full scale prototypes.

V/STOL Aircraft

Very similar to advanced ship concepts, the improved operational capabilities of future V/STOL aircraft presents an open-ended challenge to materials technology. As is well known, the vertical/short takeoff and landing (V/STOL) capability provides the Navy with the option of deploying combat aircraft from a greater number of smaller, less costly and more responsive carriers and ships with air-launch capability. Some estimates predict a majority V/STOL aircraft inventory for the Navy and Marine Corps near the turn of the century. Similar to the high performance ships, the

range and payload of V/STOL aircraft are curtailed relative to conventional carrier aircraft. The most direct approach to improving the operational effectiveness of future V/STOL aircraft is the introduction of improved materials and design concepts in either or both the airframe and the engine.

In the case of the airframe, a revolutionary use of advanced composite materials is projected for future V/STOL aircraft. Basically, an advanced composite consists of high strength/stiffness fibers bonded in a polymeric or metallic binder (matrix). The relationship between structural weight reduction and percent of composite materials are shown in Fig. 2. Notwithstanding the efforts of the other services and NASA in composite materials development, the Navy's F-18 lightweight fighter and the Marine Corps' AV-8B advanced harrier (V/STOL) represent the state-of-art usage of advanced composites in airframe structures. As indicated in Fig. 2 the projected use of advanced composites in next generation of V/STOL aircraft truly represents a radical departure in aircraft structural design. The projected weight saving will make the useful load/total weight ratio of V/STOL aircraft approximately equivalent to that of conventional aircraft.

The development of thermostructural materials for high temperature engine applications is also a viable approach to improved operational capabilities of V/STOL aircraft. The basic goal here is to increase range and/or specific thrust (HP/lb) by a lower specific heat rate turbine operation. This can be accomplished by (1) an increase in turbine inlet temperature or (2) a reduction of air volume used for cooling. As shown in Fig. 3 significant gains in gas turbine efficiency have been made over the past three decades by combinations of the two approaches. The payoff in air cooling, however, is considered to be one of diminishing return. Realization of higher inlet turbine temperature, therefore, equates with increasing the allowable metal temperature for turbine components above the current 1000°C limit of superalloys (Fig. 3).

Because of the complexity of high temperature service behavior of thermostructural materials and because of the critical consequences of engine failure, the introduction of new materials will be more evolutionary than revolutionary in nature. Nonetheless, the payoffs are significant. For example, a simple extrapolation of the trend shown in Fig. 3 indicates a 300°C increase in turbine inlet temperature before the turn of the century. Depending on type of engine, this increase equates to a 10 to 30% increase in specific thrust.[1,2,3]

Conventional Ships

Notwithstanding the development of high performance ships, V/STOL aircraft and other advanced concepts, it is a reasonable assumption that the majority investment in the fleet inventory at the turn of the century will be derivatives of current ship designs. Although the development of these systems will also be evolutionary in nature, the potential impact of structural material technology is no less diminished. The supposition is supported by the large number of systems which benefit from improvement in

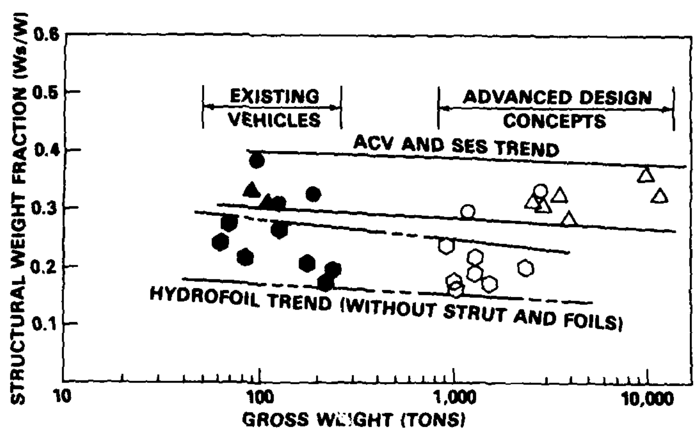


Fig. 1 Comparison of structural weight fraction versus gross weight for existing (closed symbols) and advanced design concepts (open symbols); air cushion vehicles, ACV, O; surface effect ships, SES, △; and hydrofoil, ⬡.

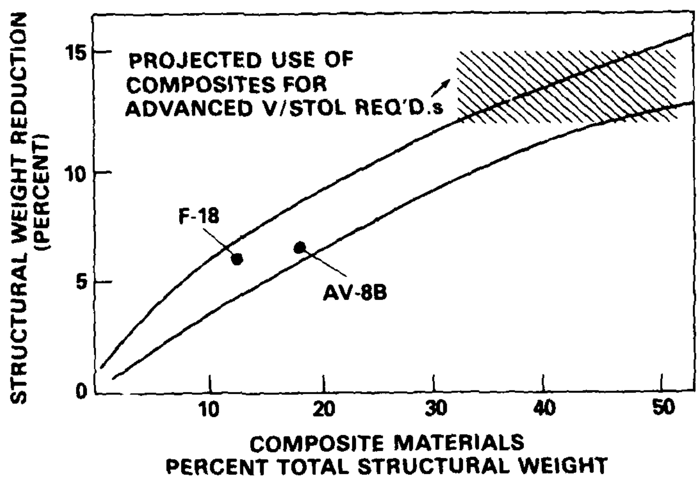


Fig. 2 Relationship between structural weight reduction and composite material usage in advance airframe structures. Projected use of composite materials for advanced V/STOL requirements indicated.

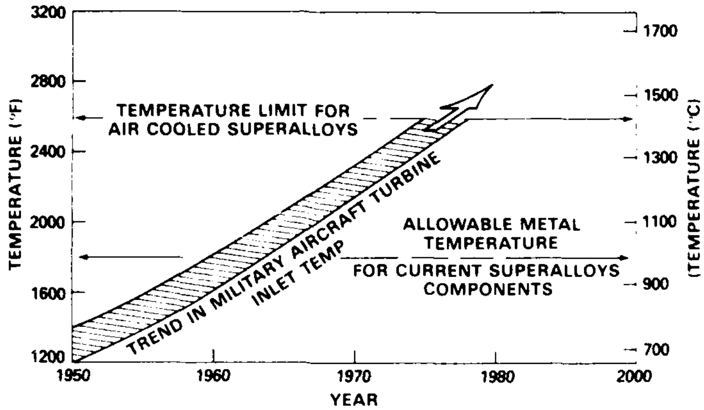


Fig. 3 Trend in military aircraft turbine inlet temperature; and allowable metal temperature for current superalloys.

materials technology. Moreover, current trends indicate a shift of R&D priorities and emphasis from performance requirements to other factors affecting military-worth, such as damage tolerance and survivability, availability, and that nemesis of all defense systems-costs.

The requirement for improved damage tolerance and survivability was made apparent in the 1975 collision of the aircraft carrier John F. Kennedy and the cruiser BELKNAP. The melted remains of the cruiser's aluminum superstructure are shown in Fig. 4. Only the steel frame remains erect. The lightweight aluminum superstructure of conventional ships is a post World War II innovation and, therefore, has not been combat tested. Moreover, fire hazard susceptibility as well as ballistic damage tolerance were also cited as issues in the combat worthiness of the predominantly aluminum construction of advanced surface ships. Hence, the continual development and innovative use of affordable fire resistant coatings, insulation materials, lightweight armor and improved structural materials are required to sustain the improved performance obtained by aluminum alloys in ship construction.

Another example of the potential impact of structural materials technology on the operational capabilities of conventional ships is the marine gas turbine engine - the adopted prime mover for U.S. Navy non-nuclear surface ships. Because of prohibitive cost associated with the development of an altogether new engine design, the U.S. Navy's design approach has been to modify an existing aircraft turbojet engine.[2] Previous experience indicates that the life limiting factors of marine gas turbines are hot corrosion of components in the high temperature section. Accordingly, the major modifications in the so-called "marinizing" of the aircraft engine are

Fig. 4 The fire damage of the aluminum superstructure of the cruiser BELKNAP after collision with the aircraft carrier JFK in 1975.

the substitution of more corrosion resistant alloys and coatings and the reduction of the maximum operating temperature. Similar to aircraft engine design, the decrease in operating temperature results in a performance penalty.

Although the marinizing approach is prudent in terms of economic and engineering considerations, early sea trials of the resulting prototype engine revealed an unanticipated form of severe corrosion attack of the turbine blade at low power operations. In contrast to the more common hot corrosion which gives significant attack above 1550 °F, the low power corrosion occurred at temperatures in the range of 1200 - 1400°F and limited blade life to an unacceptable duration.[4] Subsequent improvements in the blade coating and the filtering and ducting system has increased blade life to an acceptable level of 5000 hours.

Nonetheless, the aggregate effect of hot corrosion in the low and high power operation reqimes remains as the life limiting factor of the marine gas turbine. Accordingly, the introduction of improved hot corrosion resistant alloys and coatings into the hot sections directly equates to increased engine life and correspondingly increased availability of the host platform. Moreover, improvement in hot corrosion resistance of these components will be insurance against other contingencies, such as premature degradation of the filtering system by improper maintenance or operation or by emergency/wartime damage, as well as the potentially harmful effects of substandard (e.g., high sulphur) or synthetic fuels.

The above commentary on high performance ships, V/STOL aircraft, and conventional ships is intended to illustrate the structural materials requirements of far-term, next generation, and operational systems, respectively. These discussions could have included other important and equally materials dependent systems, such as submersible, missiles, amphibious and armor vehicles. Rather than extend these discussions adinfinitum, however, attention is now directed toward technical issues and R&D opportunities associated with high strength marine alloys. As previously noted, the topics selected for review in the following sections are considered representative of structural materials developments with near-to-far-term impact. (In addition, these topics compliment well other U.S. papers at this seminar)

R&D OPPORTUNITIES FOR IMPROVED PERFORMANCE OF HIGH STRENGTH MARINE ALLOYS

Technical Issues

Notwithstanding the positive gains made in the utilization of advanced organic composite materials over the past decade and the optimistic forecast for the development of metal matrix composites, it is a reasonable assumption that the vast majority of structural material utilized in high performance naval applications will be derivatives of current ferrous, aluminum and titanium base alloys. Moreover, the major technical issue in developing improved alloy systems (or even in the optimum utilization of existing alloys) is the ability to predict and control an exacting trade off of their engineering properties and service behaviors.

As is well known, the structural efficiency of alloys and weldment systems is directly proportional to allowable design stresses at which these materials can be incorporated into a structure. The design stress for high strength alloys, however, are typically a fraction (1/5 to 1/2) of the yield strength which in turn are only a fraction of the strength which is metallurgically obtainable. The seemingly conservative (low) design stresses of high strength alloys are dictated by their defect and cracking sensitivity in the marine environment (for example fracture toughness, stress corrosion cracking, fatigue, corrosion fatigue, etc.) as well as their general corrosion resistance.

A quantitative example of the relationship between strength, crack tolerance and corrosion resistance for a precipitation hardened stainless steel (17-4PH) is given in Fig. 5.[5] This alloy has been utilized for specialized purposes in aircraft and rocket components and in certain marine applications like struts and foils for hydrofoils because of the alloy's relatively good corrosion resistance at high strength levels. The data of Fig. 5 show the effects of electrochemical potential coupling on the stress corrosion cracking resistance of this alloy, heat treated to various strength levels. Stress corrosion cracking (SCC) resistance of an alloy is related to the initiation and growth of a crack at stress concentration sites in the presence of a corrosive environment, and is measured by the fracture mechanics parameter K_{ISCC}. This parameter defines a threshold crack-tip stress state below which SCC will not occur in the test environment. Usually, the critical stress intensity value of K_{ISCC} for SCC is determined experimentally from sustained-load tests conducted on relatively small precracked specimens immersed in saltwater.

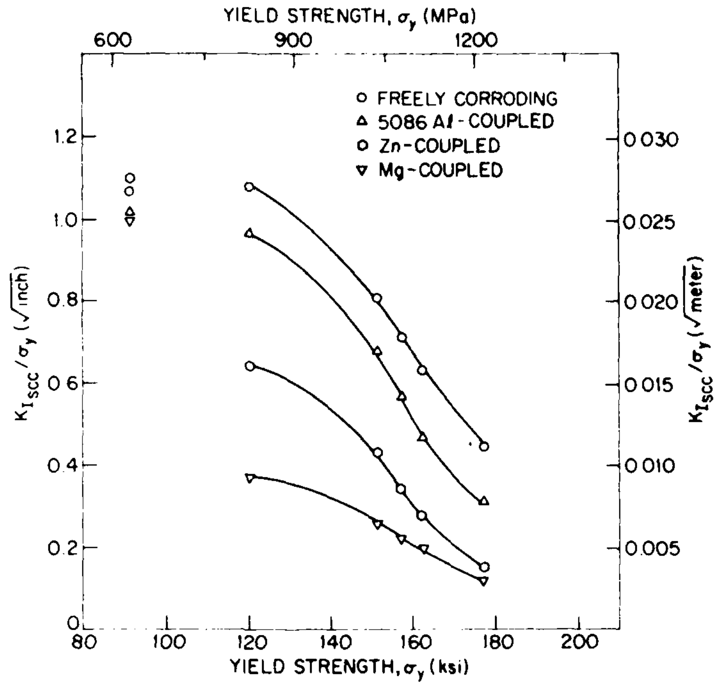


Fig. 5 Stress corrosion cracking data for high strength stainless steel (17-4PH) of different yield strengths under four electrochemical conditions (Ref. 5)

The upper curve of Fig. 5 illustrates the decrease in SCC resistance for increasing strength levels under freely corroding conditions. The lower curves show the effects of changing the electrochemical potential by coupling to aluminum, zinc and magnesium. The coupled materials are similar to anodes used in corrosion protection of marine structures.

If the positive directions of the horizontial and vertical axes of Fig. 5 are equated to increased performance (strength) and increased structural reliability (K_{ISCC}) respectively, and if the negative coupling parameter is equated to decreasing maintenance costs (corrosion protection), these data are indicative of the materials selection trade-offs facing the designer of marine structures. Namely, what windows in Fig. 5 represent the optimum utilization of an alloy in specific applications? In addition, this type of materials characterization, when coupled with improved understanding of the basic mechanism of SCC, will also provide a basis for the development of improved alloys as well as improved fabrication and inspection techniques.

An even more quantitative example of the engineering significance and trade offs of strength and crack tolerant behavior of high strength alloys in a marine environment is given in the data of Fig. 6. Here measured values of

the critical stress intensity factors for plane strain fracture toughness, K_{IC}, and for stress corrosion cracking thresholds, K_{ISCC}, for steels and titanium alloys have been plotted as a function of the measured yield strengths and the calculated critical depths for a thumb nail type surface crack in a large, unaxial stressed plate. In accordance with the fracture mechanics relationship between stress σ and critical crack depths dc ($K_{IC} \sim \sigma\sqrt{dc}$) loci of constant stress intensity factors are shown as line of constant slope on these log-log plots.

The data sets shown in Fig. 6 were abstracted from the literature[6] and are considered representative, but by no means definitive, examples of the crack tolerant behavior of these important class of structure alloys. Hence, no quantitative conclusions should be inferred from these data analyses although several broad brush trends can be observed. Namely, the crack tolerant behavior of these alloys is seen to depend on their strength and is seen to be extremely sensitive to the aqueous environment.

Through heat treatment, the yield strength of these alloys can be varied over a wide range of values. Increases in strength, however, are accompanied on the average by a greater than proportionate decrease in the plane strain fracture toughness. As defined by the ASTM Standard E399, the plane strain fracture toughness is a material-toughness property measured in terms of stress-intensity factor of a linear elastic medium. In this test procedure, K_{IC} is based on the lowest load, that is lowest stress intensity, at which a significant extension of the crack occurs. Hence, the K_{IC} points of Fig. 6 indicate the critical crack depths at which the hypothetical flawed plate will fail under yield stress loading. Because of square dependence of the critical crack size on K_{IC}, the fracture susceptibility of a component is disproportionately increased as the yield strength of the alloy and/or operating stress are increased. For example, the critical crack size for the structural alloys decreased by an order of magnitude over the ranges of yield strength examined.

The data for two recently developed alloys, NAVAIR's CORONA-5 (Ti-4.5Al-5Mo-1.5Cr) and Air Force's AF1410 steel (Fe-14Co-10Ni-2Cr), are shown respectively in the data sets of Fig 6. Both alloys were developed to meet the needs of aerospace applications based on fracture mechanic design criteria[6] and represent significant increase in fracture toughness relative to these 1972 data bases.

As previously defined, the K_{ISCC} data of Fig. 6 indicate the critical crack depth at which a crack will grow when the hypothetical flawed plate is immersed in an aqueous solution (3.5% NaCl) and subjected to a yield stress loading. The value are seen to be anywhere from 2 to 100 times smaller than the critical crack sizes for fast fracture in identical materials.

By far the smallest critical defect sizes of Fig. 6, is related to the so-called fatigue stress intensity threshold, K_{TH}. Here the critical size of defects, several orders of magnitude less than those which cause fast fracture, is determined by a lower bound stress intensity factor which must

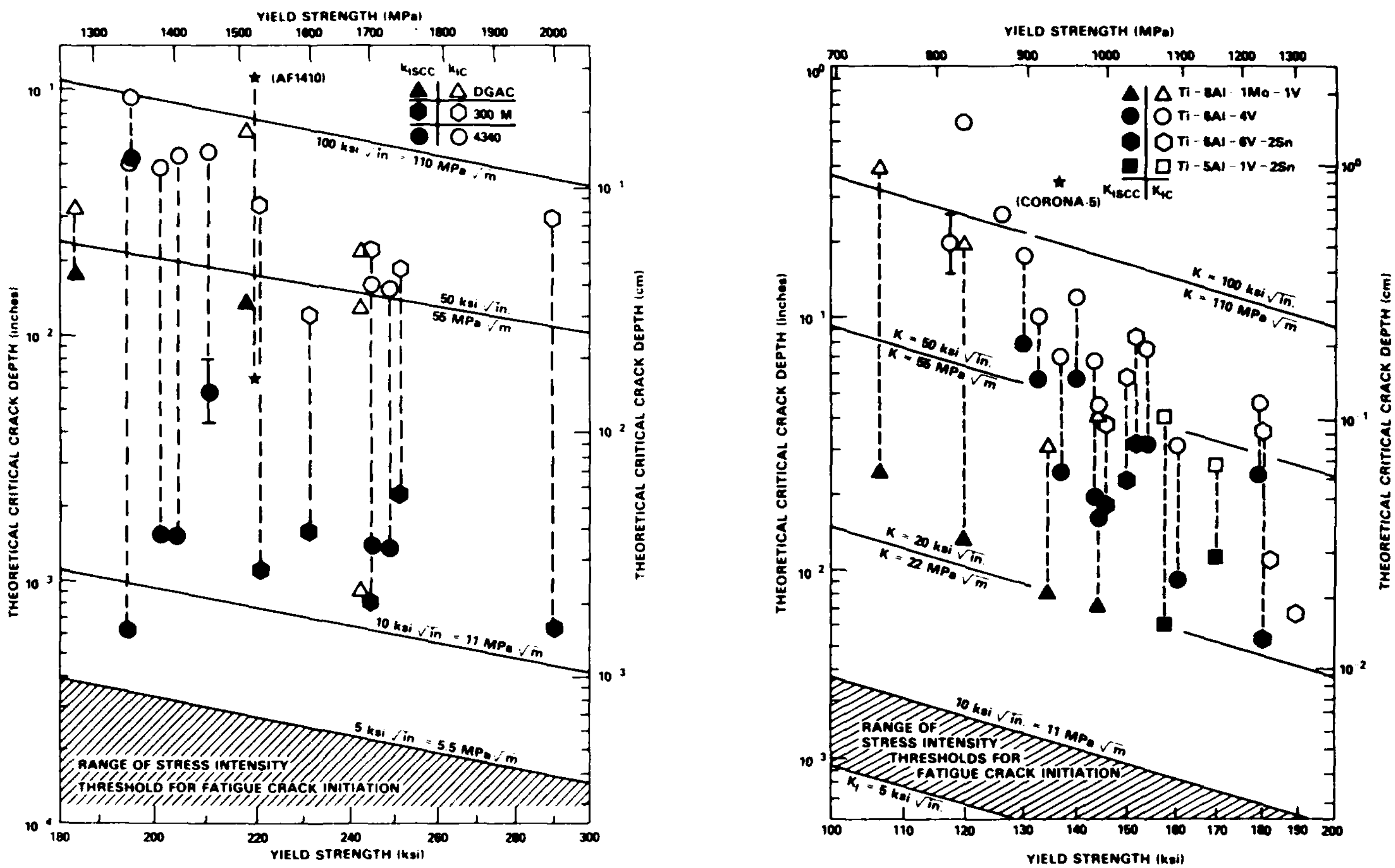


Fig. 6 Fracture Toughness (K_{IC}) and Stress Corrosion Thresholds (K_{ISCC}) data for martensitic steels and α-β titanium alloys are plotted as function yield strength and theoretical critical crack depth for a hypothetical uniaxial stressed plate under a yield stress loading (Ref. 6).

be exceeded for fatigue crack to proprogate. Although the continuum assumption of fracture mechanics is suspect at this size scale, e.g., cracks less than 0.001 cm, these extrapolations do indicate the extreme cracking sensitivity of high strength alloys. It is also of interest to note that the smallest size surface flaw which can be reliably and routinely detected by state-of-art nondestructive inspection techniques in a production line environment is usually in excess of 0.1 cm.

The data analyses of Fig. 5 and 6 not only illustrate the engineering trade offs which must be considered in the design of high strength alloy components and structures, but also are indicative of a critical element in the development of improved alloy systems, that is the capability to quantitatively predict the service performance of high strength alloys. Indeed, by combining the predictive capabilities of advanced fracture mechanics and electrochemical analyses with modern metallurgical principles and processing procedures, it is now possible to design and tailor the properties of high strength alloys for optimum service performance. As previously cited (see Fig. 6), the AF 1410 steel and CORONA-5 titanium alloy are examples of modern alloy development based on fracture mechanics criteria. The work of Yoder and co-workers on fatigue resistance[7] of aerospace titanium alloys (Ti-6Al-4V and Ti-8Al-1Mo-1V) is also a noteworthy example of this approach. Here microstructural modification by post processing heat treatment have resulted in a 70 fold increase in the fatigue crack growth resistance of these alloys. In addition, the improvements in behavior can be rationalized in terms of the microstructural modification and the crack tip stress state as defined by the fracture mechanic stress intensity factor.

Most recently the approach of tailoring or designing alloys for specialized requirements has been enhanced with the emergence of two highly versatile techniques for surface modification of metals and alloys, namely ion implantation and laser beam processing. As described in the following sections of this paper, these techniques now provided the means to optimize the often critical surface sensitive properties including, crack initiation, general corrosion, friction and wear.

Ion Implantation

Ion implantation in metals and alloys has experienced a rapid growth during the past few years. Since the early 1970's there has been a significant number of articles, papers, books and conferences devoted to non-electronic properties of ion implanted materials[8,9,10]. Surface related properties such as friction, wear, corrosion and fatigue-life of structural metals and alloys are found to improve as a result of ion implantation. Almost all surface-sensitive, life-limiting properties of structural metals can be modified by ion implantation. Furthermore, ion implantation has several advantages such as: (1) the method is independent of diffusion-controlled processes and thus surface chemistry can be modified to any desired fluence with any chemical species, (2) bulk properties related to strength and toughness can be maintained at the desired values while optimizing the surface chemistry and microstructure without a sharp interface, and, (3) use of relatively scarce metals can be minimized through surface alloying by ion implantation.

Ion implantation is a process of electrically accelerating ions to high velocities and directing them into the near-surface regions of metals and alloys to produce in essence a different alloy in the near-surface region. The method can indeed be utilized to produce a graded alloy from the surface to the unchanged underlying bulk. Since the method is distinctly different from coating or plating processes, there are no problems relating to adhesion or change of microscopic dimensions. The apparatus consists of an accelerator which produces a high energy ion beam (usually at tens to hundreds of kilovolts) of any preselected element. These ions are forcibly injected beneath the surface of any material. This injection process produces an intimate alloy of the implanted and the host elements without producing a sharp interface characteristic of all coating processes. The resultant depth distribution and alloy composition depend on the energy and the atomic number of the projectile as well as on the atomic number of the host.

Typically, depths of hundreds to thousands of angstroms are achievable with concentrations of up to 50%. Since it is not a thermodynamic process, metastable alloys can be formed without regard for solid solubility or diffusivity. However, if chemical equilibrium is required, it can be achieved by a suitable post heat-treatment. Depending on the characteristics of the host metal and the implanted ion, metastable phases including amorphous structures could be formed on the surface of crystalline substrates.

Fatigue Behavior: Early preliminary measurements on the effects of ion implantation on fatigue properties are reported by Hartley[11]. Here rotating bend tests on smooth, polished specimens of stainless steel and titanium exhibited an eight to ten fold increase in fatigue life after a 200 keV, 2×10^7 per cm^2 implantation of nitrogen (N^+) ions. Similar improvements were also observed[11] for flat specimens of maraging steel implanted with 2×10^{17} per cm^2 carbon dioxide ions (CO_2^+) and tested under high cycle fatigue conditions. It was also reported that the implanted specimens, in contrast to the unimplanted specimens, experienced a significant temperature rise immediately before fracture. Following a suggestion by Thompson[12], it is speculated that this effect is related to excess strain energy caused by the impediment of dislocated motion in the implanted layer. Evidence to support such a conjecture, however, are unavailable at this time.

Rotating bend tests have also been reported[13] on low-carbon steel (AISI 1018) specimen implanted with 75 keV, $2\times10^{17}/cm^2$ nitrogen ions. As shown in Fig. 7, the fatigue life time of the nitrogen-implanted specimen exhibited a larger variation than the unimplanted samples but no discernible overall improvement. However, a substantial improvement in nitrogen samples were measured (column 3 of Fig. 7) after the specimens were room temperature aged for approximately 4-months or artifically aged at 100°C for 6 hrs., (column 4 of Fig. 7). This aging treatment allows both the relaxation of residual surface stresses and the diffusion of nitrogen to depths three to four time the as implanted depth of 0.1 micrometer. Subsequent transmission microscopic study showed that large concentrations of 10nm precipitates of

$Fe_{16}N_2$ form at the near surface region of the sample and presumably delays crack nucleation. Further investigation is required to establish the mechanism for the observed fatigue life improvement. To this end, it may be useful to compare the fatigue life and microstructure of the nitrogen implanted alloy with those of conventional nitriding.

Ion implantation has also been shown[14] to produce beneficial effects on the fatigue behavior of α-β processed Ti-6Al-4V alloy. As shown in Fig. 8, implants of either carbon or nitrogen ions of 75 keV and $2x10^{17}$ atoms/cm^2 improves the high cycle fatigue life of this alloy as evidenced by the increase in the endurance limit above unimplanted results. These data are for rotating beam fatigue tests of 1600cpm. In addition, the carbon implantation data of Fig. 8 shows a significant improvement in the low cycle fatigue behavior. In contrast to the previously discussed results for low-carbon steel, heat treatment has only a small effect on the fatigue behavior of either type of implanted specimens.

Microstructural modification of the Ti-6Al-4V alloy from the prescribed nitrogen and carbon implantation were studied[14] by transmission electron microscopy. In the case of the nitrogen implants, the structure consisted of a dense, poorly resolved damaged layer, with no indication of a second phase. At the same dose level, however, carbon implantation produced a high density of second phase particle of approximately 10 to 20nm (Fig. 9a). After heat treatment of one hour at 400°C in ultra high vacuum, the second phase particles density is increased, and the size range is now 20 to 50nm (Fig. 9b). Selected area diffraction pattern analysis of second phase particles indicate the crystal structure to be titanium carbide (TiC). Reportedly, the occurrence of second phase particles for the carbon but not the nitrogen may be attributed to the lower solubility and higher mobility of carbon over nitrogen in titanium.

A noteworthy feature of the nitrogen implanted and unimplanted Ti-6Al-4V fatigue specimens was revealed through examination of the fracture surfaces by the scanning electron microscope. For all specimens where the life time exceeded $2x10^5$ cycles, the initiation site of the fatigue crack was between 25 and 150 micrometer below the surface. Such subsurface cracking in titanium alloy has been observed by others[15]. Because the depth of the implanted layer is less than 0.1 micrometer, it was concluded that the N^+ implantation has little or no effect on the crack initiation site but, nonetheless, does inhibit the crack growth toward the surface.

Corrosion: Ion implantation has been shown to have a profound effect on the corrosion of a variety of metals and structural alloys, including titanium, stainless steels, and aluminum. Experiments have also shown that pure iron implanted with ions of Cr and Ni exhibit corrosion resistance identical to stainless steels of comparable bulk composition. These results show that a corrosion protection layer can be formed on the surface of structural alloys without building up the concentration of the entire bulk.[16] Accordingly, the ion implantation of alloys provides a unique method of minimizing the use of supply-limited alloying elements without sacrificing properties.

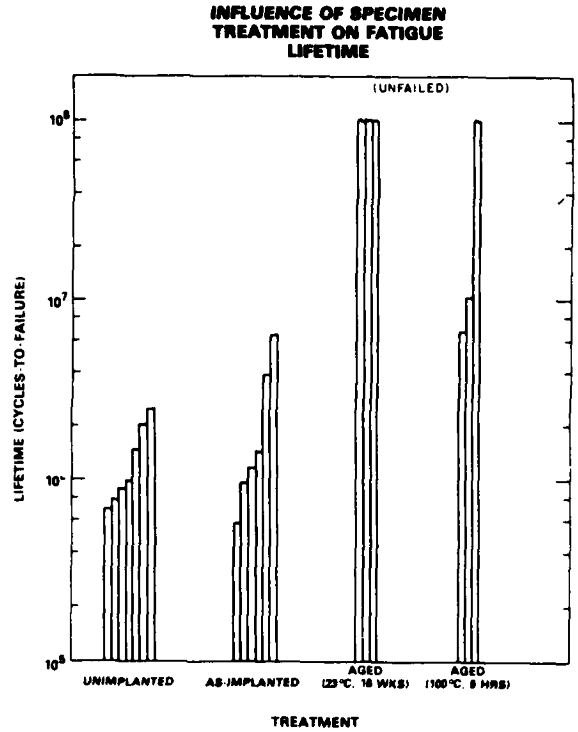


Fig. 7 Cycles-to-failure for four different specimen treatments of AISI 1018 steel. Rotating beam f:tigue at 50 ksi.

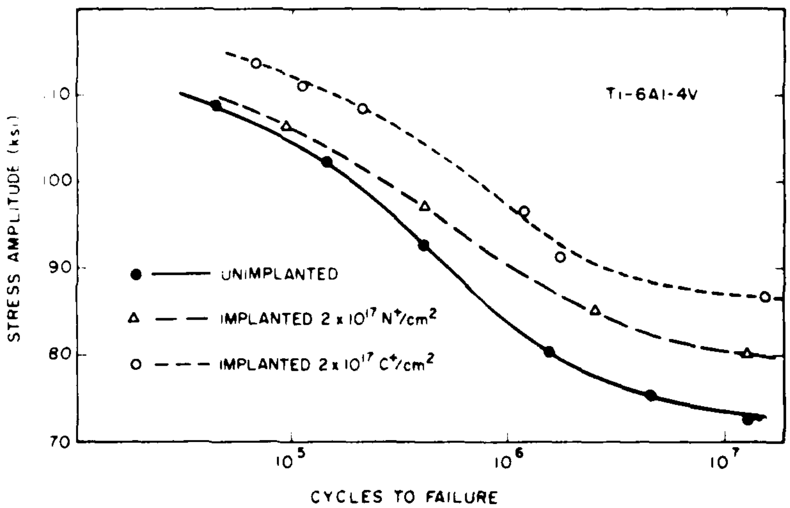
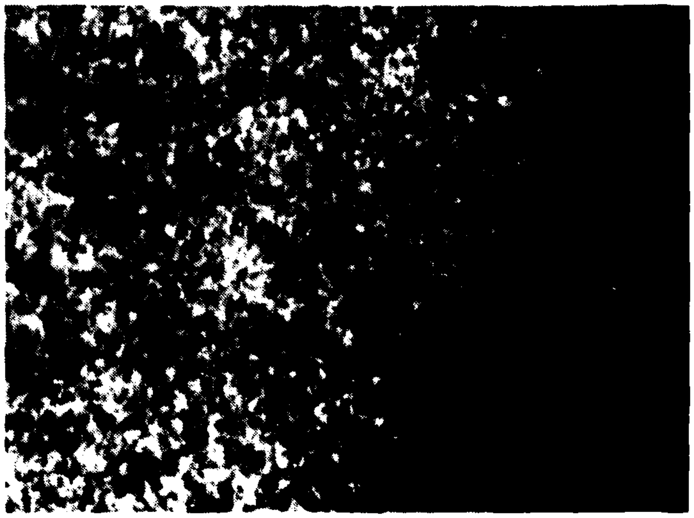
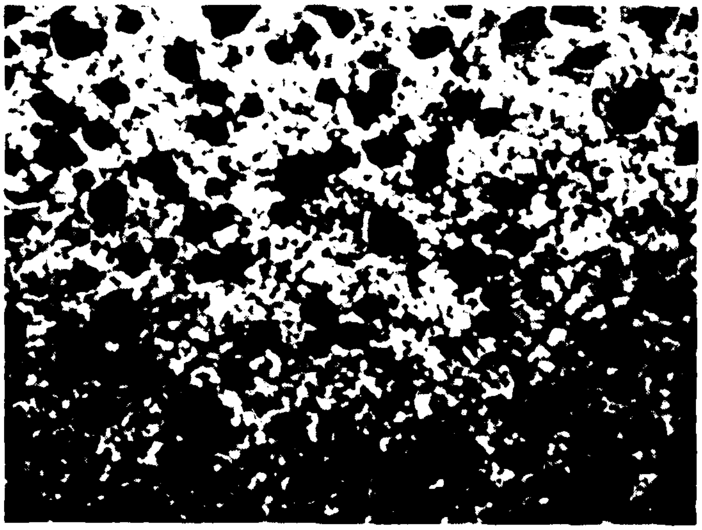


Fig. 8 Cycles-to-failure versus applied stress for Ti-6Al-4V in a rotating beam fatigue at 1600cpm.



$(\vdash\!\!\!-\!\!\!-\!\!\!\dashv)$

(a) As Implanted 2000Å



$(\vdash\!\!\!-\!\!\!-\!\!\!\dashv)$

(b) Annealed 1 Hr 400°C 2000Å

Fig. 9 Microstructures of Ti-6Al-4V Implanted 2×10^{17} AT/cm^2 Carbon Ions (C^+)

As a low-temperature process, implantation also offers potential benefits for applications where conventional, high temperature coating processes produce unacceptable bulk property changes. For example, the implantation of chromium into a commerical maraging steel has been shown[17] to improve the corrosion resistance of this alloy without changes in bulk properties. The high temperature required to apply a chromium layer by conventional diffusion processes would result in significant increase in grain size, which in turn degrades the strength and toughness of this alloy. Another example of this type is given by results of high dose chromium implantation into a AISI M50 bearing steel.[18] As shown in the macrographs of Fig. 10, the implanted alloy via the unimplanted alloy shows a significant improvement in the general and localized corrosion when tested under laboratory-simulated field conditions. Here again surface modification requiring high temperatures would unacceptably reduce the toughness of this bearing alloy. In addition, implantation produces no macroscopic dimensional changes and can be applied to otherwise finished components.

Oxidation: Beneficial effects of ion implantation on the high temperature oxidation of alloys have also been explored in a number of investigations. For example, oxidation rates of chromium rich stainless steels are significantly reduced by implantation of Yttrium and other rare earth ions[19]. Similar results have been reported for titanium implanted with Ba, Co, and Eu[20]. In this case oxidation was reduced at all temperatures. In these examples it is hypothesized that the formation of impermeable Perovskite structures, such as $YCrO_3$, $LaCrO_3$, $BaTiO_3$ inhibited thermal oxidation. In addition, reference has been made[21] to reducing the parabolic rate constant for oxidation of FeCrAlY alloy by Al ion implantation. Reportedly, this effect is related to formation of Al_2O_3 to concentrations not obtainable by bulk alloying.

Hardness: Several investigators have reported a significant increase in surface hardness of alloys resulting from ion implantation. Of course it should be recognized that these hardness values are determined by measuring the Vickers or Knoop hardness number, which consists of making diamond indentations several times deeper than the thickness of the implanted layer, and therefore, do not precisely represent the implanted surface hardness.

Most experiments have been done in pure iron or steels implanted with carbon, nitrogen, argon and boron[22,23]. In all cases the surface microhardness improved due to implantation. The observed surface hardening has been related to the probable formation of carbides or nitrides or to the radiation induced damage effects. It is interesting to note that inert gases such as Ar and Ne have no effect when implanted above 500°C, whereas room-temperature implantation produces hardening. Boron-implanted beryllium substrates show significant promise for use in precision gas-bearing components. The components currently in use have a hard oxide coating which exhibit adhesion problems.

Friction & Wear: Most of the work, all very preliminary, on the effect of ion implantation on friction has been conducted at Harwell. Measurements

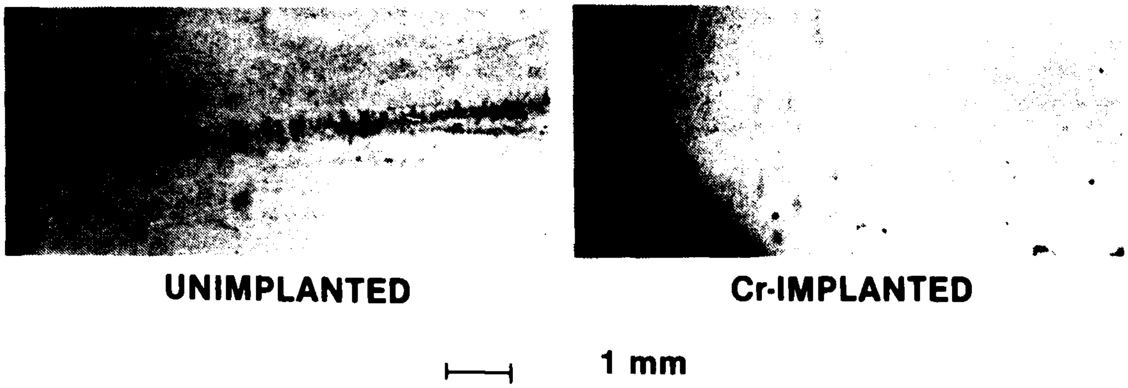


Fig. 10 Results of Laboratory - simulated field corrosion tests. When both parts were the M50 alloy, the flat surface suffered severe localized attack. A line of pits was located at the meniscus center, and additional pitting was observed in the thin layer near the edge of the flat surface. Ion implantation with Cr eliminated both areas of attack (right photograph).

of friction force between a tungsten carbide ball and case-hardened steel (IN 352) implanted with Mo, Sn, Pb, In and Kr at fluences between 10^{16} and 10^{17} ions/cm^2 show encouraging results. The results show no effect of Kr, and increase for Pb and a decrease for Sn both by as much as 50%[24].

Overlapping implantation of Mo and S significantly reduced friction presumably due to the formation of MoS_2. Ion implantation does provide a novel method of forming near-surface precipitates known for their solid-lubricant properties on a hard, wear resistant material.

Probably the most extensive study has been directed to study the improvement of wear due to ion implantation. Most of the wear tests have been carried out with a pin-on-disk test under lubricated conditons. The wear rates of the rotating implanted disks were found to be significantly reduced by as much as a factor of 30. Wear rates of several steels and bearing alloys implanted with N, C, Ar, Mo and Co has been determined by this method.

Advanced analytical techniques are currently being used for the investigation of the implantation effects on wear, including Mossbauer spectroscopy, Auger electron spectroscopy, transmission electron microscopy, scanning electron microscopy and wear particle analysis[25]. Results comparing the unimplanted and implanted couples indicate that there is no significant change in the shape or size distribution of the wear particles produced even though they differ in quantity by a factor as high as several hundred. Although the fundamental features of the responsible mechanisms are not understood as yet, the results suggest that implantation reduces the initiation and growth rates of cracks formed during the wear process.

Laser Surface Modifications

The high power densities attainable with laser beams have made possible the development of a wide range of surface modification techniques, including transformation hardening, laser glazing, surface alloying, laser cladding, consolidation of coatings, and laser melt/particle injection. Some of these techniques are adaptations of ones long popular in industry, while others were made possible by the rapid heating and cooling rates attainable with high power lasers. Transformation hardening is typical of those techniques which are adapted from earlier practice. It utilizes the laser beam to briefly heat the surface of a steel sample to austenitizing temperatures, permitting conduction cooling by the unheated base metal to quench the heated zone and produce a hard, martensitic structure on the surface. The advantages which accrue from using laser (or electron-beam) heating rather than induction or flame heating are that minimal heating of the bulk material can prevent thermal degradation of bulk metal and can limit distortion of the part during quenching[26].

Laser glazing[27] differs from transformation hardening in that the surface layer is melted, not simply cycled through a set of solid state phase transformations. The melting and rapid resolidification makes possible surface hardening, through the refinement of microstructure, of a wide range of alloy types. It can, in some alloys, improve the corrosion resistance[28] by eliminating or minimizing phase separation. Surface alloying, to be discussed in detail subsequently, can improve both the corrosion and wear resistance of a wide range of alloy types. It does so by introducing alloying elements which improve the corrosion resistance or which stabilize hard, wear resisting phases.

Laser cladding, a patented process[29], is similar to traditional weld cladding processes in that it uses the energy of the laser beam to fuse a metallic overlayer and weld it to the surface of the base metal. The material to be clad to the surface can be in the form of a loosely adhering powder or it can be wire fed directly into the weld pool. The consolidation of coatings with lasers differs from laser cladding only in the means of applying the cladding material prior to laser melting. That is, a coating previously applied by a process such as flame spraying or plasma spraying is laser remelted to remove residual porosity or to improve its adherence to the base metal[30,31]. These two processes are both suited for producing corrosion and wear resisting surfaces, and the preferred technique for any particular application is dependent upon numerous factors. In principle, the ease of applying diverse coatings by the thermal spray processes should recommend the consolidating route, but problems related to the presence of trapped gases in flame and plasma sprayed coating may limit the widespread adoption of this approach[31].

Two relatively recent developments in laser beam processing of materials are laser shock hardening[32] and laser melt/particle injection[33,34]. As its name implies, the first of these processes utilized high intensity pulsed laser beams to induce stress waves in an irradiated material and thereby harden the near surface layer. The laser melt/particle injection process can

be used to modify surfaces in several distinct ways by an in-situ composite formation. These two processes along with laser surface alloying are considered in more detail subsequently, because they offer significant potential to improve high strength marine alloys.

Laser Surface Alloying: This process consists of melting the surface of a metal workpiece, adding known amounts of other metals, mixing these components, and allowing them to resolidify. This process produces a surface layer with a chemical composition and properties which are different from the substrate material. This technique allows the surface properties of a structure to be tailored to the surface requirements without sacrificing the bulk characteristics. The surface layer is also metallurgically bonded to the substrate and provides a high degree of adhesion. Other reasons for laser surface alloying are that rapidly solidified structures are produced and that surface coverage rates of up to 1 cm^2/sec are often obtained.

There are three classes of processing conditions used to produce laser surface alloys: (1) low power density, (2) high power density, and (3) high power density but with the beam rastered at a high speed[35]. With the first approach, specially designed optics are used to obtain a beam spot with a power density of 10^3 to 10^5 W/cm^2 which is slowly swept across the specimen. The surface layer is held molten long enough for convection currents to establish themselves within the molten pool and to provide for the mixing of the components. The second class of processing conditions makes use of the plasma produced by the interaction of the laser with the melt pool to stir the pool and to mix the components. The third class is a hybrid of the first two where a high power density beam is very rapidly rastered to produce a low average power density.

Fig. 11(a) shows the cross section of a low carbon steel specimen from which a chromium steel surface alloy was made. In this case, the AISI 1018 steel was first coated with an 8μm thick layer of chromium. A focused, 5kW, CO_2 laser beam was swept across the surface at 50 cm/sec to melt the coating along with a portion of the substrate. The degree to which the components are mixed is illustrated in the chromium x-ray display of Fig. 11(b) which shows that chromium was dispersed throughout the depth of the melt.

A larger surface may be processed by using successive passes, each one of which overlaps with the previous pass. This process is illustrated in Fig. 12 where a Ti-6Al-4V surface was alloyed with molybdenum. After this single set of passes, there remains some variation in composition within the melts as indicated by the large dark arcs that result from the etching. By reprocessing the surface alloy of Fig. 11 using identical conditions, a substantially uniform composition is obtained. The result is shown in Fig. 13 where the molybdenum addition has produced a single phase surface alloy.

The electrochemical behavior of chromium steel surface alloys described above (Fig. 12) also have been reported[36] for three different conditions in de-aerated 0.1m Na_2SO_4. Each sample was immersed for 30 minutes and then

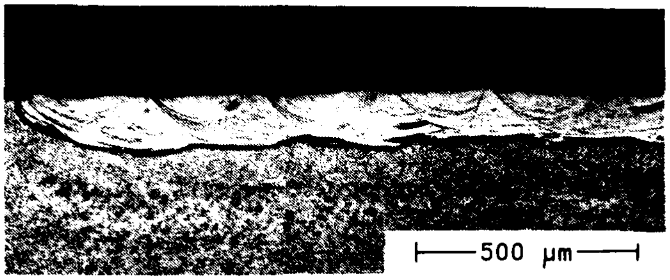
(a)

(b)

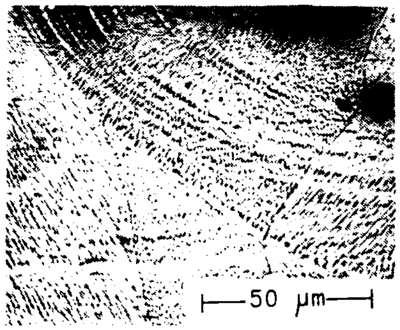
Fig. 11 (a) Polished and etched cross section of an AISI 1018 steel coupon which was coated with an 8µm thick layer of chromium and laser surface alloyed using a focused 5 kW laser swept at 50 cm/sec. (b) A chromium x-ray display of the cross section in (a).

2 kW, 30 cm/sec, 0.25 mm step, Single Coverage

Fig. 12 Polished and etched cross section of a molybdenum rich surface alloy produced by successive overlapping melts of a molybdenum coated Ti-6Al-4V specimen. The laser processing conditions are shown.



(a)



2 kW

30 cm/sec

0.25 mm step

Double Coverage

(b)

Fig. 13 (a) Polished and etched cross section of a molybdenum rich alloy first processed as the specimen in Figure 2, and then reprocessed to provide additional mixing. (b) High magnification photograph showing the columnar dendritic structure of the surface alloy in the vicinity of a melt overlap.

held cathodically at - 1.0V or S.C.E. for 5 minutes. Following this cathodic treatment, steady-state open circuit corrosion potentials were obtained by each sample after an additional 30 minutes immersive period. Anodic polarization curves were determined potentiodynamically at a scan rate of 10m V/nm.

As shown in Fig. 14 the anodic polarization curves indicate extensive dissolution of 1018 steel at all potentials, but the surface alloys passivate similar to conventional Fe/Cr stainless steels. Moreover, the current density in the passive region decreases with increasing Cr content. The laser surface alloy with highest Cr content passivates without undergoing an active-passive transition.

Although numerous other investigations on laser surface processing have been reported, property evaluations of the modified layer, with the exceptions of a few cases, have been restricted to metallurgical analysis and hardness measurements. Perhaps the most illustrative example of the potential of laser surface processing is the use of laser melting to normalize the surface of a sensitized 304 stainless steel[28]. By adjusting the cooling

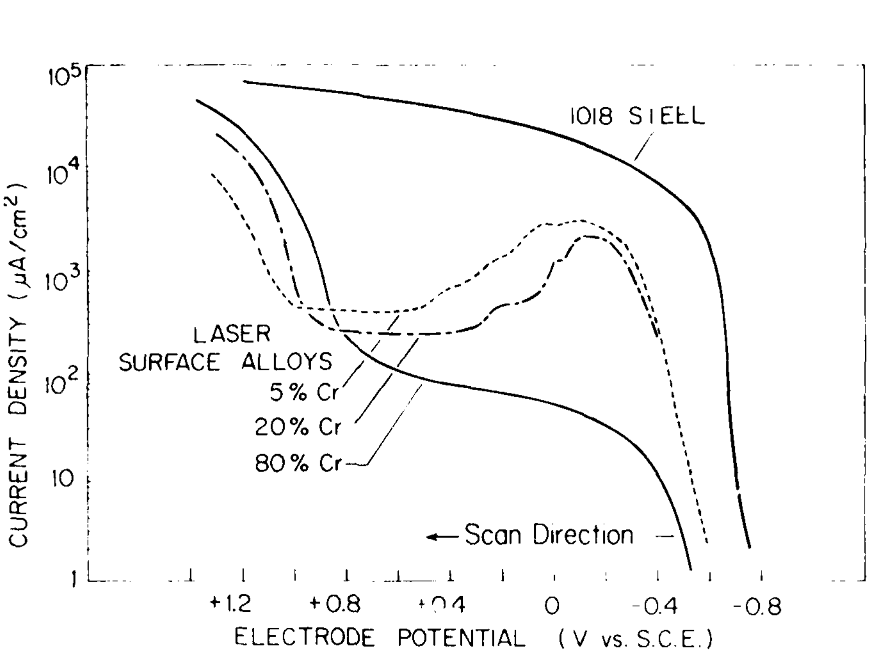


Fig. 14 Anodic polarization curves for Fe/Cr laser-surface alloys in de-aerated 0.1M Na_2SO_4.

rate to avoid a deleterous carbide phase at the grain boundary, the laser processed specimen exhibited a dramatic elimination of intergranular corrosion susceptibility and a much improved resistance to stress corrosion cracking.

Evidence has also been reported on the improved stress corrosion cracking of α-β titanium alloys by surface melt refinement[37]. In this study, rapid laser melting was used to transform the α phase to a less SCC susceptible martensitic phase. Test of the laser melted titanium specimens, however, showed that the residual stresses arising from incomplete coverage promoted stress corrosion cracking. In general, the effects of residual stresses on the cracking behavior appears to be an unresolved issue for laser processed surfaces of high strength alloys.

Metallurgical analysis of rapid laser surface melting and alloying of a variety of alloys, Zircoloy[38], martensitic and tool steels[39], and low carbon steel[40] show promise to improve their crack tolerance behavior although no crack tolerance tests were reported. This situation is in contrast to ion implantation studies where improved fatigue performance is usually presented without collative metallurgical examination.

There are several possible disadvantages to laser surface alloying. There is a certain amount of roughness introduced by the melting process and although conditions can be chosen to minimize the roughness, any application

must either be tolerant of the roughness or the surface must be refinished after laser processing[35]. A very strong crystallographic texture can be introduced by the solidification process as a result of the faster growth of grains having low Miller index planes oriented in the direction of the temperature gradient[36]. The change in texture is most pronounced with fine grained materials where favorably oriented grains will be closer together and so will more quickly squeeze out less favorably oriented grains. The most significant drawback of laser surface processing is the residual stress introduced by the rapid, localized heating of the surface. These residual stresses limit the number of materials that can be processed since many will crack as a result of the processing. Short of this, the residual stresses can cause warpage of a workpiece, require a stress relieving heat treatment, or other stress modifying treatment, such as peening. In any application these drawbacks will have to be weighed against the advantages described previously.

Two major technical issues remain to be addressed. The first is determining the best method of introducing the alloying elements. This can be accomplished either by the addition of a powder mixture, an alloy powder, or wire, directly to the melt, or by coating the specimen using traditional techniques before the laser processing. The second issue is the development of techniques for quality assurance which will insure the batch to batch reproducibility of the product.

The Laser Melt/Particle Injection Process: This process, shown schematically in Fig. 15, consists of melting a shallow pool on the surface of a sample which is translated under a focused laser beam, and of blowing powder particles into the melt pool from a fine nozzle positioned about 1 cm away. The powder can be hard, wear resisting particles which dissolve to only a limited extent in the melt, or it can be metallic particles which are deliberately dissolved in the melt to accomplish surface alloying. Alternatively, the processing conditions can be adjusted so that the beam melts just enough of the sample surface to weld down a coating which is built up from powder blown into the melt pool. For purposes of discussion in this paper, these three variations of the process will be called: (1) particle injection (when minimal dissolution occurs), (2) injection alloying (when full dissolution occurs), and (3) injection cladding (when substrate melting is minimized). Of these three variations, particle injection has been most fully explored, and most of our discussion will refer to it.

Wear resisting layers have been produced on iron, nickel, titanium, aluminum, and copper based alloys by injecting TiC or WC into their surfaces. The processing can be done as isolated melt passes of the type shown in Fig. 16, or as extended area coverage like that shown in Fig. 17. The single melt pass shown in Fig. 16 was produced by injecting TiC particles into a melt pool produced in Ti-6Al-4V. This pass employed a laser power of 6kW and a sample translation speed of 5 cm/sec. This scanning electron photomicrograph shows both the top surface of the sample and a sectional view through the melt pass. Examination of this photo will reveal a significant difference between carbide injected surfaces and wear resisting surfaces produced by coating techniques such as plasma spraying. That is, the wear resisting

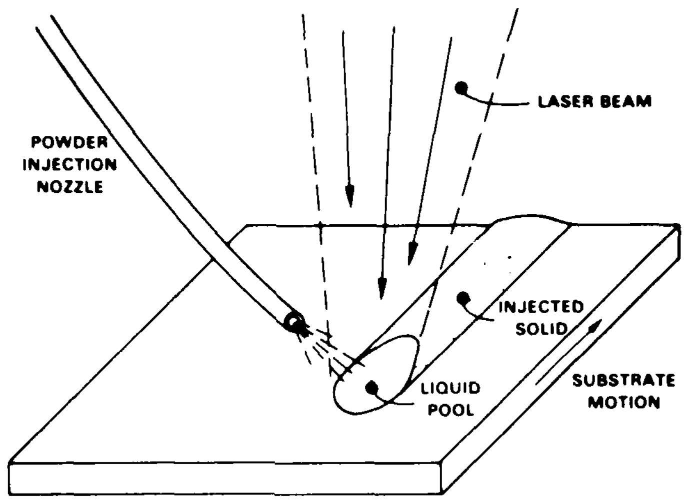


Fig. 15 Injection of particles into a melt zone established by a high power laser beam.

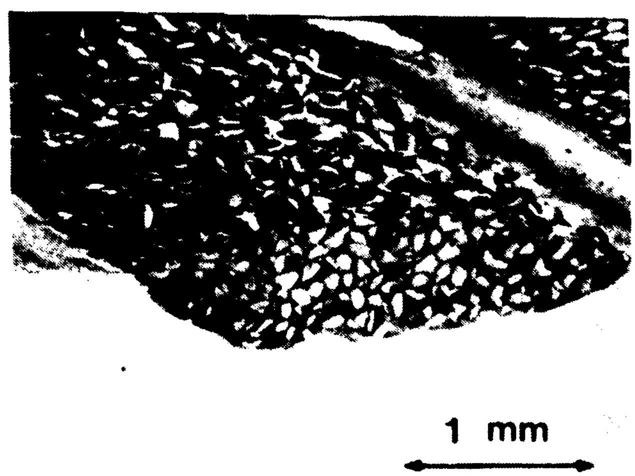


Fig. 16 Sectional view of Ti-6Al-4V sample injected with TiC particles.

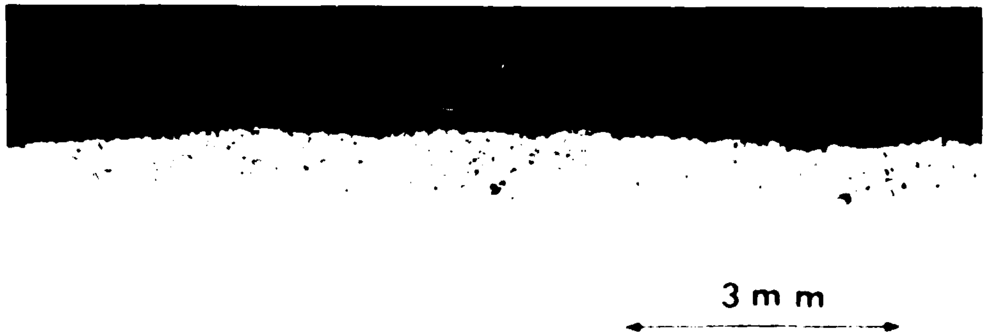


Fig. 17 Sectional view of 5052 aluminum injected with TiC in a series of overlapping melt passes.

particles are incorporated into the bulk metal, and are not simply stuck onto the surface. The advantage of this feature is that the wear resisting surface is an integral part of the material and cannot be flaked off by thermal or mechanical stress.

Extended area coverage of the sort shown in Fig. 17 is produced by overlapping single passes of the sort shown in Fig. 16. The 5052 Al sample shown in Fig. 17 was made by injecting -170+220 mesh TiC into a 3 mm wide melt pass, and by advancing the sample 1 mm after each pass under the beam. This processing produced a sample with a uniform carbide distribution, but with a relatively rough surface, as can be seen in the profile view shown in Fig. 17. For most applications smoother surfaces are required, but this presents no great difficulty because the surface can be ground and polished as shown in the two surface view of Fig. 18. This sample has a particularly uniform distribution of carbide particles in its surface as a result of the wide overlapping of melt passes. In some other carbide/metal pairs experimented with it has not been possible to get carbide distributions as uniform as that in Fig. 18 because interactions between the carbide and the metal limit the amount of overlapping which can be employed. This point will be illustrated by a discussion of the interactions which occur when TiC is injected into Ti-6Al-4V.

In Fig. 16 the metal matrix between the injected carbide particles looks substantially darker than does the unmelted base metal. This dark appearance derives from the presence of fine carbides in the metal matrix. These carbides can be seen in Figs. 19a and 19b, which show higher resolution views of a sectioned surface similar to that in Fig. 16. The large, injected carbide particles in these photos were partially dissolved in the molten Ti-6Al-4V during processing, but upon solidification the dissolved carbide partitioned out as fine TiC dendrites between the injected particles. The dendritic carbides are evident in these photos because the metal matrix originally surrounding them was etched away. The metal matrix, still evident between the dendrites, is believed to be very similar in composition to the

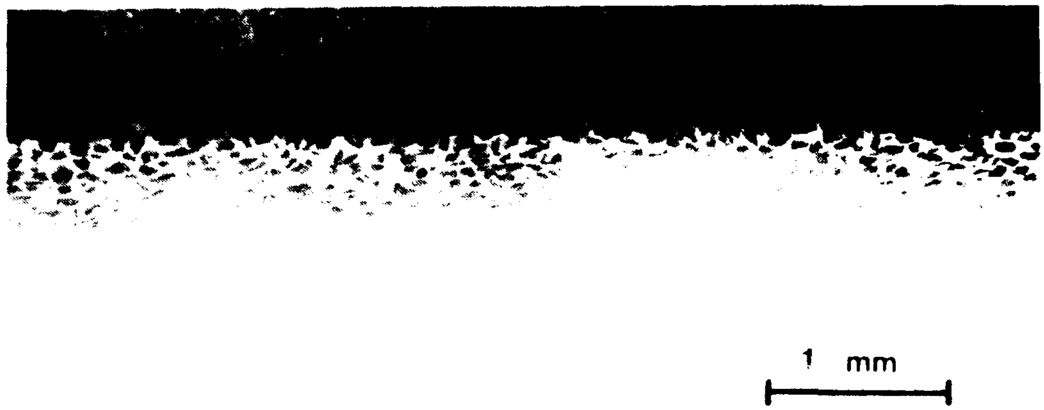


Fig. 18 Sample shown in Figure 17, after surface was ground and polished.

base Ti-6Al-4V. This partial dissolution and repartitioning of carbides in Ti-6Al-4V and in other transition metal alloys experimented with is of importance because it tends to embrittle the metal matrix. When this occurs, thermal stresses produced during processing can cause cracks to form in the hardened surface layer.

The major technical issue to be resolved with regard to application of this process is determination of the best way to limit this crack formation. One approach to this problem is to limit the opportunity for dissolution by minimizing the amount of overlap between melt passes. Fig. 20 demonstrates such an approach for TiC injected into Ti-6Al-4V. One can see from the photo that this approach leads to a less uniform distribution of carbide particles in the surface, but for some applications this may not be critical. Other possible approaches to limit particle dissolution are to employ spheroidized carbides thereby minimizing surface area and reducing the number of crack initiation sites[41], or to precoat the injected particles with a film of a material with limited solubility in the melt.

As mentioned earlier, the laser melt/particle injection process can also be used to accomplish injection alloying and injection cladding. Neither of these variations has yet been explored in any detail, but results to date indicate that both approaches offer potential advantages over established techniques. The principle advantage in both variations is that the surface modification can be accomplished in one processing step. That is, no precoating or elaborate surface preparation is required. Further study may well show additional advantages.

<u>Laser Shock Processing</u>: Another processing surface modification technique which has shown improved crack properties of high strength alloys is laser-shock processing. When exposed to the output of a high intensity pulsed laser, typically 10 watts/cm^2 with pulse duration between 20 and 70

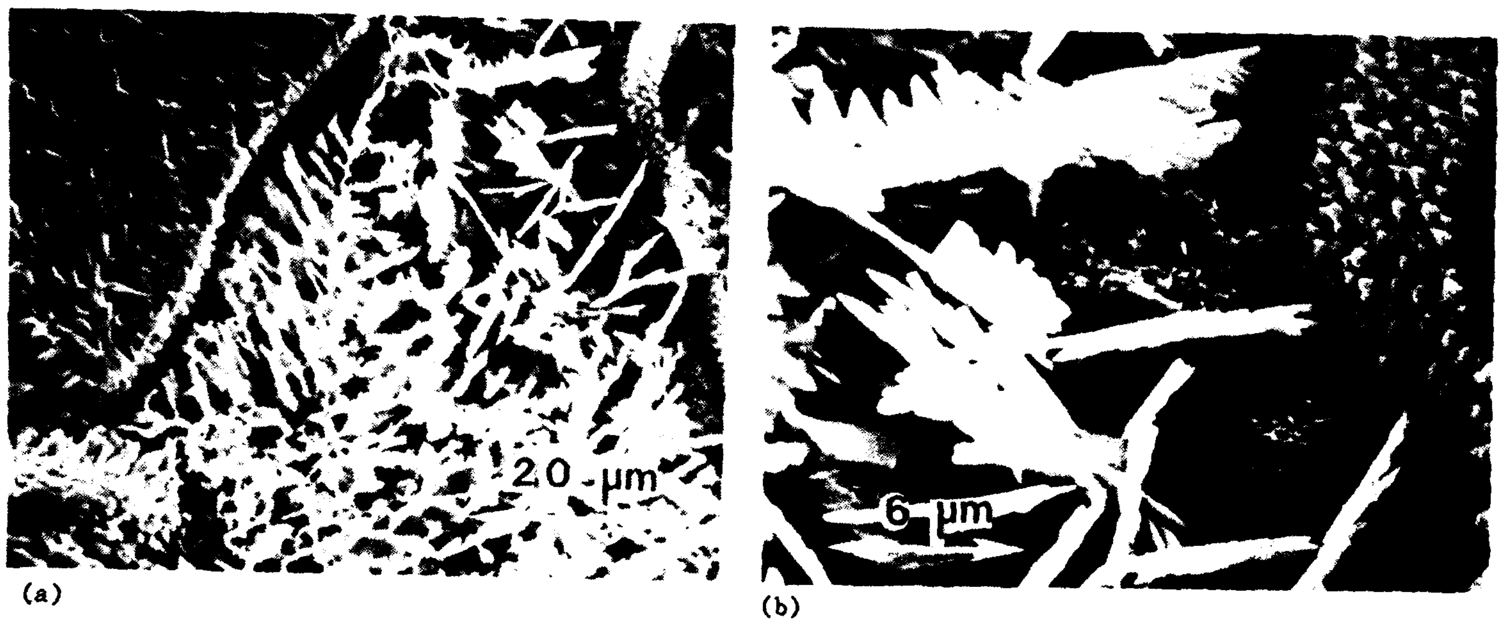


Fig. 19 Fine dendritic TiC within Ti-6Al-4V matrix injected with coarse TiC.

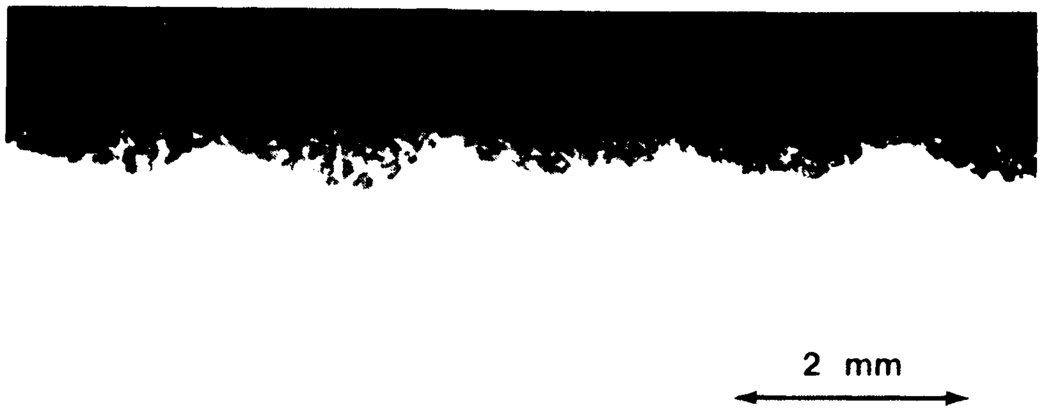


Fig. 20 Sectional view of Ti-Al-4V sample injected with TiC. Surface was ground flat after injection processing.

macroseconds, stress waves are induced into an irradiated material[42]. This reaction is generated by the extremely rapid vaporization of the irradiated material and the subsequent expansion of the heated vapor against the target surface. In comparison to the magnitude and velocity to conventional flyer plate generated shock waves, laser induced stress wave should be classified as weak shock, typically reaching peak pressures of less than a kilobar. Methods of amplifying laser induced stress to high pressures are achieved by placing opaque and transparent overlays on the test piece. The benefits of laser shock hardening relative to other methods of shock hardening or conventional work hardening is not clear, although the laser technique has been shown to be one of the most useful methods for treating localized or inaccessible areas.

Laser-shock processing has been shown[43] to increase the yield strength and to a lesser extent the ultimate strength of age-hardenable aluminum weldments, 5086-H32 and 6061-T6, and of solid solution strengthened aluminum alloys, 7075-T6 and 2024-T35. The fatigue crack initiation resistance, the fatigue crack growth resistance, and the data scatter have been shown to be significantly improved by laser-shock processing[32]. Using this technique, data has also been reported on an increased fretting fatigue resistance of 7075-T6 fastener joints[44]. The above results suggest the use of laser shock processing to improve the strength and fatigue properties of critical areas of structures, such as welded joints and highly stressed regions.

SUMMARY STATEMENT

The intent of this paper has been to present representative examples of the requirements, issues, and opportunities facing the Naval structural materials community over the next several decades. In order to keep the paper to a tractable length, many equally important topics, including those associated with strategic missile, space systems, and other marine structures, were omitted reluctantly and any priority of effort should not be inferred by omission herein.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the helpful discussion and written imputs to this paper from their colleagues at the Naval Research Laboratory, including Dale Meyn, Ron Vardiman, Peter Moore, Bhakta Rath, Jim Hirvonen, Jack Ayers, Ed McCafferty, George Yoder, Tom Crooker, and Bob Jones.

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